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14. ABSTRACT

A number of mutually-coordinated cofacial edge-over-edge metalloporphyrins have been sythesized and characterized by UV-visible, resonance Raman, time-resolved absorbance, nonlinear absorbance, fluorescence and NMR spectroscopic methods. Both homometallic and heterometallic dimers have been isolated. Excited state triplet absorbances of the dimeric complexes are red shifted, toward the second harmonic emission wavelength of Nd:YAG. In spite of the diminished singlet excited state lifetimes of these complexes relative to their monomeric counterparts, this shift results in significant nonlinear absorbance at 532 nm due to the increased triplet absorption cross section at that wavelength. Serveral dimers have been characterized by resonance Raman spectroscopy. The most interesting part of these spectra is in the low-frequency region where they contain bands not found in the spectra of the monomeric porphyrins. These bands have been analyzed in the context of intra-dimer vibrations.

15. SUBJECT TERMS

porphyrin, nonlinear optics, spectroscopy

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Final Report

Award #F49620-96-1-0359

Objectives

The objectives of this project remain as stated in the original proposal

Status of Effort

The following is the final report of accomplishments towards the goals of our project to synthesize, characterize and investigate the nonlinear optical (NLO) properties of cofacial porphyrin assemblies. In year one of this project, we generated a number of porphyrin precursors, asymmetrically-substituted porphyrins and their metalloporphyrin complexes, carried out preliminary studies on the aggregate structures, and built some of the laser-based instrumentation needed for the time-resolved and NLO spectroscopic aspects of the project.

During the second year, we made strides toward both synthetic and spectroscopic goals of the project. We synthesized a number of new dimeric and oligomeric porphyrin compounds. We carried out initial spectroscopic characterization of the ground and triplet excited states of the well-characterized dimeric complexes. The spectroscopic signatures of the dimers have been compared with those of their monomeric analogs in an effort to understand the electronic effects of cofacial aggregation. A simple and inexpensive spectrometer was developed for the determination of nonlinear absorbance response curves. This device has been used to measure the optical limiting curve of one of our dimeric complexes. A major limitation in this work was the inability to obtain large amounts of the asymmetrically substituted porphyrin ligands required for assembly of the mutually-coordinated metalloporphyrin oligomers.

In the third and final year, we were compelled to pour efforts into optimizing the synthetic protocols for of the asymmetrically-substituted porphyrin ligands. Through this focused effort, we made incremental progress in increasing the yields. Improved yields notwithstanding, the spectroscopic aspects of the project were still limited by sample availability.

Accomplishments/New Findings

Ligands & Metal Complexes

We have obtained compelling evidence that the solution structures of our 2-pyridyl-bridged Mg(II) and Zn(II) complexes are dimeric and that they are of the partially cofacial edge-over-edge type, as illustrated in Figure 1. The dimers are stabilized by mutual coordination of their coordinating *meso* substituents. The evidence for this structure comes from solution NMR spectra, resonance Raman spectra and exogenous ligand titrations. The proximity of the cofacial porphyrin rings results in excitonic coupling of the porphyrin chromophores, which results in new states that are accessible via optical transitions. The most striking effect of this coupling is the splitting of the porphyrin-based B band ($S_0 \rightarrow S_2$ π-π^* transition) into two bands separated by >800 cm^{-1}. Although we have been unable to grow diffraction-quality single crystals for solid-state structural determination, the strong intra-dimer excitonic coupling suggests small inter-planar spacing in these complexes that is likely near the van der Waals contact distance for cofacial aromatic rings (3.4 Å).

Early studies of the mutually-coordinated metalloporphyrins such as the one shown in figure 1 revealed that, while the 2-pyridyl group is capable of coordinating to a partner metal center ($K_d \sim 10^{-9}$), the resulting dimeric complexes are easily disaggregated by aromatic or polar solvents. We have been able to increase the stabilities of these complexes by putting 5-membered heterocyclic ligands at the meso positions of the porphyrin. These include 2-imidazolyl and 2-thiazolyl moieties. Metallation of the imidazolyl and thiazolyl porphyrin ligands affords mutually coordinated complexes with dimeric edge-over-edge structures. These dimers are much more stable than their 2-pyridyl counterparts, probably due

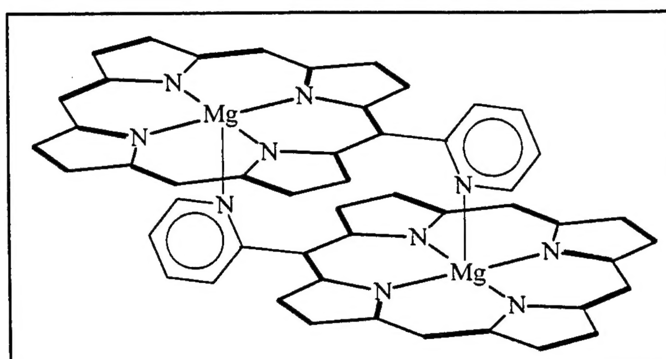

Figure 1. Mutually-coordinated magnesium 2-pyridylporphyrin. Each porphyrin contains three additional *meso*-4-alkylphenyl substituents, which have been omitted to clearly show the edge-over-edge structure.

to increased basicity of these heterocycles and less imposition of steric strain upon mutual coordination to the 5-membered rings. Their stabilities are sufficiently large that they are difficult to determine accurately because of the low concentrations required to dissociate the dimers. Using the Zn(II) complex of the 2-imidazolyl porphyrin, we were able to estimate the stability using fluorescence anisotropy. Stabilities of these dimers are about two orders of magnitude higher than their 2-pyridyl counterparts. Other potentially coordinating substituents include 3-pyridyl 2-imidazolyl, 2-thiazolyl and 2-thiophenyl groups. We are currently devising an emission method to determine their stabilities using dilute solutions.

Metallation of the 3-pyridylporphyrin ligand with Zn(II) yielded a virtually intractable solid. We have obtained UV-visible absorbance spectra from very dilute solutions, which suggest that there is some excitonic interaction between porphyrin rings. This, along with the low solubility of the complex, is consistent with a partially cofacial oligomeric solution structure.

We have also characterized a Mn(III) dimer and heterometallic Mg(II)/Zn(II) and Mn(III)/Zn(II) dimers. Chemical and spectroscopic evidence suggests that all of these complexes have the same structural motif as the Zn_2 and Mg_2 dimers. The Mn(III)/Zn(II) dimer is unique in having diamagnetic and paramagnetic halves. We synthesized this complex with the goal of using ^{1}H- and ^{2}H-NMR spectroscopy to probe spin delocalization from the paramagnetic Mn(III) half to the diamagnetic Zn(II) half. Current evidence suggests either direct spin delocalization between the porphyrin π systems or, more likely, a mechanism involving direct interaction of d_π orbitals of one porphyrin and a porphyrin π orbital of its partner. The goal of these experiments is to gain a fundamental understanding of this delocalization that will support synthetic strategies for controlling intra-dimer polarization by an optical electric field.

Metalloporphyrins containing meso-2-pyrrolyl and meso-2-thiophenyl groups showed no detectable evidence of mutual coordination.

Excited-State Absorption Spectra & Optical Limiting

We have now established that the visible triplet π-π^* absorptions of our mutually coordinated Mg (II) and Zn(II) 2-pyridylporphyrins are red-shifted by 25 to 35 nm relative to their 4-coordinate monomers and 10 to 15 nm relative to their monomeric pyridine complexes. This shift results in an increased overlap of the strong triplet absorption with the weak ground state absorption at 532 nm.

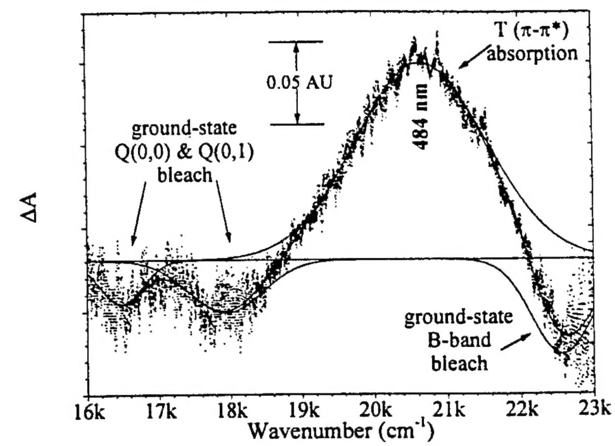

Figure 2. ΔA spectrum showing λ_{max} of the triplet π-π^* transition for a $[Zn(PyP)]_2$ in toluene. This transition is red shifted from its monomeric analogues.

Consequently, we made initial optical limiting measurements with these complexes at 532 nm. Figure 2 shows the results of these measurements. The threshold laser fluence for nonlinear absorption is approximately the same as that for a number of metallophthalocyanines, in spite of the fact that dimeric structure substantially diminishes their singlet excited state lifetimes. The dimer solutions are, however, quite sensitive to O_2 under strong laser illumination. This result will soon be submitted for publication with acknowledgment of support by this grant.

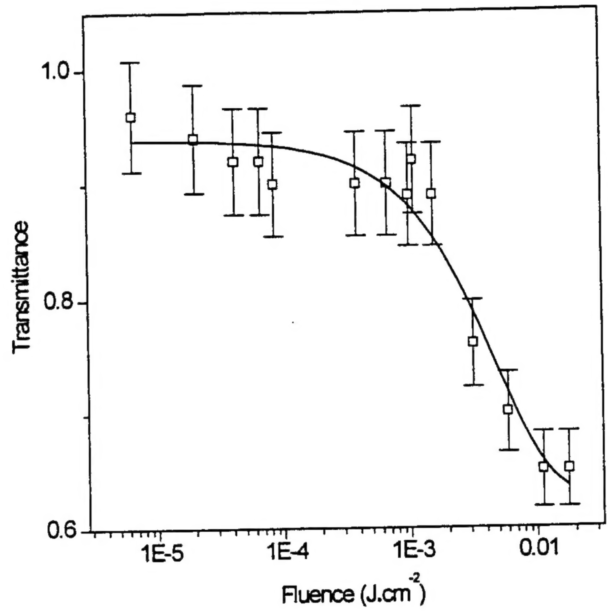

Figure 3. Transmittance vs. laser fluence at 532 nm for $[Zn(TMPyP)]_2$ in toluene.

Resonance Raman Spectra

We have recorded resonance Raman (rR) spectra of mutually-coordinated 2-pyridyl- and 2-imidazolyl porphyrin dimers containing Zn and Mg centers. Spectra were recorded using excitation in each exciton band in the blue and violet regions of the visible spectrum. We have assigned the Zn-Py stretching vibration in monomeric Zn(TPP)Py at 159 cm^{-1} using deuterated pyridine.

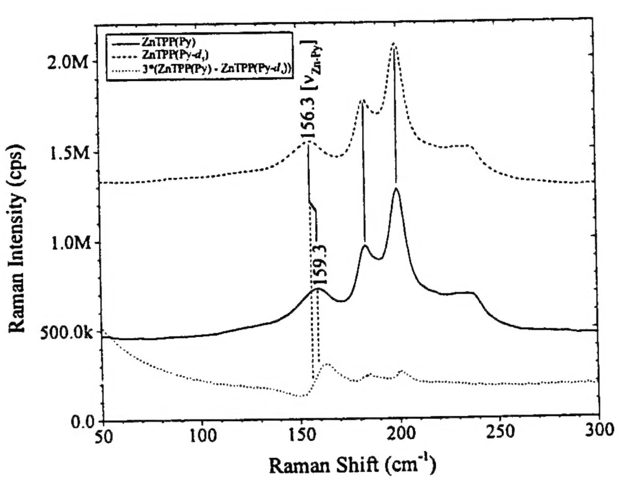

Figure 4. Resonance Raman spectra of Zn(TPP)Py showing the Py-d_5 isotope shift allowing assignment of the Zn-Py stretching vibration.

The Zn-Py stretching band is replaced by three lower-frequency bands in spectra of the mutually-coordinated dimer.

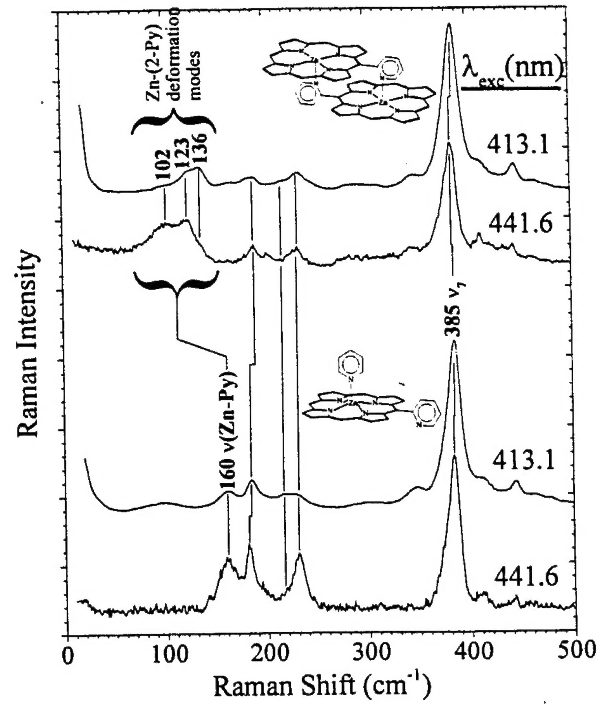

Figure 5. Resonance Raman spectra of the illustrated Zn(II) porphyrin complexes excited at 413.1 and 441.6 nm. Three meso-4-alkylphenyl groups have been omitted from the structures for clarity. The ν_{Zn-Py} band in the monomer spectra is replaced by three Zn-Py deformation bands in the dimer spectra.

These bands are assigned to the Zn-Py deformation modes of the dimer. There should be six such modes, but since the dimer is centrosymmetric, only three of the six are expected to be Raman allowed. They are illustrated in Figure 5. Three rR bands are observed at similar frequencies for the meso-2-imidazolyl analogue.

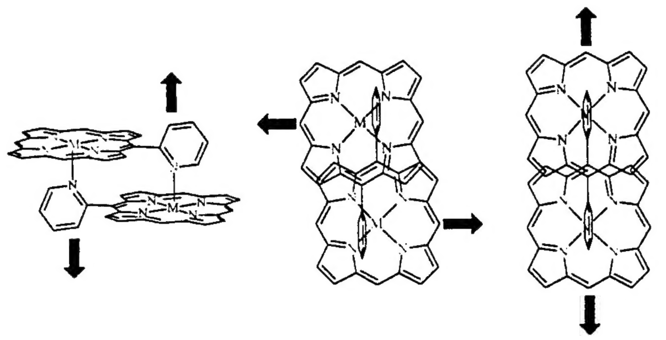

Figure 6. Qualitative illustration of the eigenvectors for the three Raman-active Zn-Py deformation modes in the mutually-coordinated dimer corresponding to the top two spectra in figure 4.

We propose that the three lowest-frequency bands in the rR spectra of the dimer (Figure 4) correspond to these three vibrational modes. These results will soon be submitted for publication with acknowledgment of support by this grant.

Potential Air Force Applications

Our dimeric compounds hold promise as chromophores for optical limiting materials. Materials incorporating chromophores of this type could be useful in protection of visible imaging sensors and human eyes against the second harmonic emission (532 nm) from Nd:YAG lasers.

Personnel Supported

Name	Position/Title
Dr. Kenton R. Rodgers	Principal Investigator
Dr. Andrei Mokhir	Postdoctoral Fellow
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Kevyn Smith	Graduate Student
Lei Tang	Graduate Student
Christina Bulisco	Undergraduate Student
Dr. Gudrun Lukat-Rodgers	Research faculty

Publications

This grant is acknowledged on the following publications.

"Synthesis and Characterization of Mutually-coordinated dimeric Cofacial Magnesium Porphyrinates," Nikolay N. Gerasimchuk, Andrew A. Mokhir and Kenton R. Rodgers, *Inorg. Chem.* **1998**, *37*, 5641-5650.

"Homometallic and Heterometallic Mutually-coordinated Zn(II) and Mg(II) Porphyrins" Nikolay N. Gerasimchuk and Kenton R. Rodgers, in preparation.

"Synthesis and Characterization of Mutally-coordinated Mn(III) Porphyrins: Solution Structure and Intra-dimer spin Delocalization" Andrew A. Mokhir and Kenton R. Rodgers, in preparation.

"Resonance Raman Spectroscopy of Mutually-coordinated Zn(II) and Mg(II) Porphyrins" Kenton R. Rodgers and Aruna Viswanathan, in preparation.

Holland, P. L.; Rodgers, K. R.; Tolman, W. B. "Is the Bis(μ-oxo)dicopper Core Capable of Hydroxylating an Arene?" submitted to *Angewante Chemie*.

Holland, P. L.; Wilkinson, E. C.; Mahapatra, S.; Rodgers, K. R.; Que, L.; Tolman, W. B. "Resonance Raman Studies on the Bis(μ-oxo)dicopper Core" submitted to *J. Am. Chem. Soc.*

Presentations of This Work

1) Department of Chemistry, University of Wisconsin at La Crosse, Seminar, 11-96.
2) Department of Chemistry, University of Wisconsin at River Falls, Seminar, 11-96.
3) AFOSR/ONR Optical Materials Program Review Conference, Jacksonville, Florida, 6-97.
4) Fargo Conference on Main Group Chemistry, Fargo, ND, Poster, 6-98.
5) Fargo Conference on Main Group Chemistry, Fargo, ND, Poster, 6-98.
6) Gordon Research Conference on Chemistry & Biochemistry of Tetrapyrroles, Salve Regina University, Newport, RI, Poster, 7-98.
7) Department of Chemistry, North Dakota State University, Seminar, 9-98
8) American Chemical Society National Meeting, Boston, MA, Talk, 9-98.

9) American Chemical Society National Meeting, Boston, MA, Poster, 9-98.
10) American Chemical Society National Meeting, Boston, MA, Poster, 9-98.

Consultative & Advisory Functions

None

Transitions

None

Inventions & Patents

None

Honors/Awards

The PI received a Presidential Early Career Award for Scientists and Engineers in December 1996. This award was based on the PI's work in the area of protein-based biological O_2 sensing.